SYNOPSIS
FOR Ph.D. IN Chemistry
(FACULTY OF SCIENCE)
B. N. Mandal UNIVERSITY, Madhepura

"A Kinetic Study of the Comparative Solvent of Aquo-Acetone and Aquo Ethanol Solvent Systems on the food Additive Efficiencies of Ethyl Heptanoate Ester"

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SYNOPSIS

i. **A Kinetic Study of the Comparative Solvent of Aquo-Acetone and Aquo Ethanol Solvent Systems on the food Additive Efficiencies of Ethyl Heptanoate Ester**

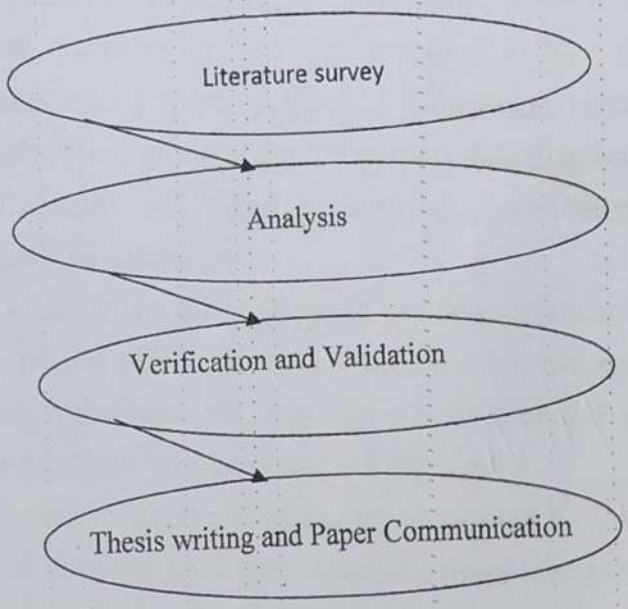
ii. **Work Plan –**

(a) Purpose and need of the society

In order to highlight the research work of the kinetic field it has been proposed to study the alkali catalysed hydrolysis of ethyl heptonoate ester in water-Acetone (Water-dipolar aprotic) and water ethanol (water-protic) reaction media, as this research seems to be of scientific importance in synthesing pharmaceutical and food additive in the form of flavouring agent. Thus this research will also help in manufacturing food additives and medicines for treating digestive disorder.

Expected outcome of the proposed research work is that the solvolysis product of the heptanoate ester i.e. heptanoic acid finds its use for manufacturing heptanoate, pharmaceuticals and artificial flavour which are very-very useful for the modern society.

Organization of work elements



(b) Details of the Project with Chapterization

The Ph.D. Thesis presenting "A Kinetic Study of the Comparative Solvent of Aquo-Acetone and Aquo Ethanol Solvent Systems on the

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food Additive Efficiencies of Ethyl Heptanoate Ester" shall be prepared in five different chapters as mentioned below:

(i) Introduction

The kineticists working on the topic "Kinetic Study of different solvolysis reactions on the basis of their observations have inferred that the externally added organic co-solvent in aqueous media have been found to affect the rate, mechanism and other thermodynamic extensive properties of the solvolysis reactions by altering the forces between reacting species which depends on the solvation power.

The activation parameters, the energy of activation (ΔE^*) and entropy of activation (ΔS^*) are dependent on the solvent nature, nature of the reaction and structure of the substrate, and therefore, they have been often employed for mechanism interpretations. The energy of activation ($\Delta E*$) is characteristic of the substrate and does not change rapidly with the change in solvent, as does the entropy of activation (ΔS^*). The later generally govern the rate of a reaction in solution. In general, the entropy of activation has been found to be more positive, i.e., less negative for S_N1 as compared to S_N2 process. For substrates which react by the S_N1 mechanism, increase in the size of the alkyl group at central carbon atom frequently leads to a positive shift in S^{*5}, but in case of S_N2 mechanism opposite effect may be found.

Effect of selective solvation on rates and mechanisms, solvation and ionisation effects of the solvent on rates, solvent effects on different types reactions, e.g., ion-ion, ion-dipolar and dipolar-dipolar reactions will be discussed separately.

The chapter in thesis presented by us headed as "Introduction" will deal with the upto date survey of literatures concerning the work of previous researchers in the field of chemical kinetics. It will also be provided with the "Research Objectives" at the end.

(ii) Literature Review –

On the ground of details survey of literatures available on the

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kinetic study on the solvolysis of ester having longer carbon chain it has been found that the heptonoate ester on hydrolysis produces heptanoic acid as the main product having straight chain of 7 carbon atoms and it is used as pharmaceutical intermediate in pharmaceutical industries. It is also used as a food additive in the form of fragrance and flavouring agents. It can also be used in cosmetic industries as surfactant, emulsifier, stabilizer and fragrance agent.

Though a large number of researchers on the solvent effect on various types of solvolysis reactions having ester as a substrate have been reported but studies on the solvolysis of the ester having longer carbon chain and its hydrolysis product possessing flavour producing and other efficiency have not been reported till now.

(iii) Experiment –

The second chapter "Experimental" will explore the experimental techniques adopted during the course of study of the kinetics of reaction including purification of the organic solvents, esters and the reagents used. In addition method of calculating rate constants and various thermodynamic activation parameters will also be included into it. The techniques for checking the precision and reliability of the experimental data will also be included into it. The different temperatures rising from 20 to 40°C, at which the kinetics, will be studied will be maintained using a water-thermostate fitted with electronic relay.

Under this section different methods for purifying the solvents and esters will be given in detail. This chapter will prepare the base for further study during the research work and will contain the methods

(a.) to evaluate specific rate constants and molar thermodynamic activation parameters of the reaction so that controlled solvolysis of the ester may be carried out for obtaining flavour of desired intensity.

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(b.) to evaluate the number of water molecule involved in the formation of activated complex for establishing the mechanistic pathways followed by the reaction in both the reaction media.

(c.) to test the validity of Barclay-Butler rule and also to evaluate the iso-kinetic temperature of the reaction in order to highlight the solvent solute interaction in both the reaction media.

(iv) Results and Discussions –

Under this heading the results obtained after studying the kinetics of alkali catalysed hydrolysis of ethyl heptanoate in (i) aquo-acetone and (ii) aquo-ethanol medium will be discussed and interpretation of the results obtained will also be discussed in two different chapters III and IV.

Both of these chapters III and IV will consist of discussion regarding the effect of solvent on specific rate constants variation of rates with mol% of solvents acetone and ethanol, the effect of dielectric constants of the reaction media, participation of water molecules on the activated complex, will be discussed for deciding the mechanism of the reaction. Effect of organic co-solvents will also be discussed separately on iso-composition and iso-dielectric activation energies (E_C and E_D) and also on the thermodynamic activation parameters such as $\Delta G^*, \Delta H^*$ and ΔS^*. Obeyancy of Barclay-Butler rule will also be tested for iso-kinetic temperature of the reaction in the reaction media.

(v) Conclusion –

Ester of having longer carbon chains are found in the joints of small animals like goats, sheeps etc hence the proposed work has interdisciplinary relevance with the subject – zoology of the science faculty.

In the end of the thesis a brief summary (conclusion of the research work) and discussion on the results will be included in Chapter V of the thesis.

(c) Hypothesis:-

For a given medium the decrease in entropy is greater for a

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small ion than for a large ion because the smaller ion is more highly solvated than the larger ion. The loss in entropy may also result when the solvent molecules are frozen around the ionic transition state. Besides Hughes and Ingold who have achieved a great triumph in the advancement of knowledge about the solvent effect on reaction rates, other workers have also tried in this field to assign a definite quantitative value to parameters of reactants and solvents determining the rate and have obtained correlation equations.

(d) Methodology

For quantitative measurement of the progress of the proposed work, i.e., for studying the kinetics of alkali catalysed hydrolysis of ethyl heptanoate the concentration of liberated acid at different interval of time will be measured by using either of the following methods -

(i) Conductivity measurement method by using digital conductivity set.

(ii) EMF measurement by setting hydrogen electrode using digital potentiometer.

(iii) titration method using Baryta Set of having standard Baryta Solution it has also been planned.

(e) Bibliography –

In addition to the consulted past references the recent references related to proposed work of the kinetic field are:

1. Benson S. W.: "The Foundation of Chemical Kinetics", Mc Graw Hill, New York, 1960.
2. Hine, J. B.: "Physical Organic Chemistry", Mc Graw Hill, New York, 1962.
3. Amis E. S.: "Solvent Effect on Reaction Rates and Mechanisms", Academic Press, New York, 1966.
4. Fross A. A. and Pearson R. G., "Kinetic and Mechanism", Wiley Edition New Delhi, 2nd Ed., 1970
5. Kumar, K. and Singh, R. T.: Effect of DMSO on the ..... solvolysis of caproates, IJESM, Jan., 2018, 7, No. (1), 535-542

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6. Singh Atulit: "A kinetic study ..... Solvolysis of Caproate Ester", Wutan Huatan Jisuan Jishu, Nov., 2019, XVI, No (XI), 354-358

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